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(54) Amide modified epoxy resins.

(57) Curable amide modified epoxy resins are prepared by polymerizing (I) the reaction product of (A) the reaction product of (1) an epoxy resin having an average of more than one 1,2-epoxy group per molecule and an average of from 0 to 30 aliphatic hydroxyl groups per molecule such as a diglycidyl ether of bisphenol A and (2) (a) a monoalkanolamine such as monoethanolamine and (b) a dialkanolamine such as diethanolamine wherein (a) and (b) are added sequentially with (a) being added first or as a mixture with (B) an anhydride of an unsaturated dicarboxylic acid such as maleic anhydride with (II) a polymerizable ethylenically unsaturated monomer or mixture of monomers such as a mixture of styrene and methacrylic acid. The resultant resin can be employed as is in the preparation of organic solvent borne coatings or it can be neutralized with a base so as to improve its stability in the preparation of aqueous coatings.

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AMIDE MODIFIED EPOXY RESINS

The present invention pertains to amide modified epoxy resins which are suitable in the preparation of coatings and the like.

The coatings industry is constantly seeking ways and means to eliminate or reduce the amount of organic solvents released into the atmosphere. Therefore, it is desirable to employ water dilutable resinous compositions in the preparation of such coatings. The present invention provides a resin which when neutralized with a base becomes water soluble or water dispersible thereby resulting in stable solutions or dispersions.

One aspect of the present invention pertains to a curable amide modified epoxy resin prepared by reacting the reaction product of (A) the reaction product of (1) at least one epoxy resin having an average of more than one 1,2-epoxy groups per molecule and an average of from zero to 30 aliphatic hydroxyl groups per molecule and (2) (a) at least one dialkanolamine and (b) at least one monoalkanolamine wherein components (a) and (b) are added sequentially with component (a) being added first or components (a) and (b) are added as a mixture; with (B) at least one anhydride of a saturated or an ethylenically unsaturated dicarboxylic acid; and wherein the components are employed in quantities which provide (i) a ratio of moles of component (A-2-a) to epoxy equivalent contained in component (A-1) of from 0.55:1 to 0.95:1, preferably from 0.75:1 to 0.9:1; (ii) a ratio of moles of component (A-2-b) to epoxy equivalent contained in component (A-1) of from 0.05:1 to 0.45:1, preferably from 0.1:1 to 0.25:1; (iii) a ratio of the combined moles of components (A-2-a) and (A-2-b) per epoxy equivalent contained in component (A-1) is from 0.9:1 to 1.45:1, preferably from 1:1 to 1.1:1; and (iv) a ratio of moles of component (B) to moles of component (A-2-b) of from 0.75:1 to 1:1, preferably from 0.9:1 to 1:1.

Another aspect of the present invention pertains to a curable amide modified epoxy resin prepared by polymerizing (I) the reaction product of (A) the reaction product of (1) an epoxy resin having an average of more than one 1,2-epoxy group per molecule and an average of from zero to 30 aliphatic hydroxyl groups per molecule and (2) (a) a dialkanolamine and (b) a monoalkalanolamine; wherein the components (a) and (b) are added as a mixture or sequentially with component (a) being added first; with (B) an anhydride of an unsaturated dicarboxylic acid; with (II) a polymerizable ethylenically unsaturated monomer or mixture of monomers; wherein (i) the ratio of moles of component (I-A-2-a) to epoxy equivalent contained in component (I-A-1) is from 0.5:1 to 0.95:1, preferably from 0.75:1 to 0.9:1; (ii) the ratio of combined moles of component (I-A-2-b) to epoxy equivalent contained in component (I-A-1) is from 0.05:1 to 0.5:1, preferably from 0.1:1 to 0.25:1; (iii) the ratio of combined moles of components (I-A-2-a) and (I-A-2-b) to epoxy equivalent contained in component (I-A-1) is from 0.9:1 to 1.5:1, preferably from 1:1 to 1.1:1; (iv) the ratio of moles of component (I-B) to moles of component (I-A-2-b) is from 0.75:1 to 1.25:1, preferably from 0.9:1 to 1.1:1; and (v) component (II) is present in quantities which provide from 5 to 75, preferably from 10 to 50, most preferably from 15 to 30 percent by weight based upon the combined weight of components I and II.

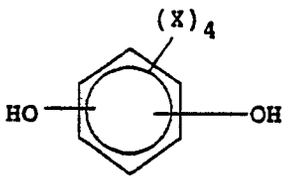
Another aspect of the present invention pertains to a water soluble or water dispersible product resulting from neutralizing the aforementioned amide modified epoxy resins with a base.

Another aspect of the present invention pertains to coatings prepared from said amide modified epoxy resin and to coatings prepared from said neutralized amide modified epoxy resin.

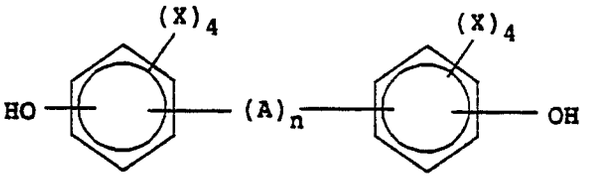
The reaction between the epoxy resin and the mixture of primary and secondary amines can be conveniently conducted at a temperature of from 25°C to 200°C, preferably from 60°C to 150°C. If desired, the reaction can be conducted in the presence of a suitable reaction medium such as, for example, aliphatic or aromatic hydrocarbons, ketones, glycol ethers, alcohols, ethers, esters, and combinations thereof. Particularly suitable solvents which can be employed as a reaction medium include, for example, methanol, ethanol, isopropanol, butanol, cyclohexanol, 2-butoxyethanol, 2-methoxyethanol, 2-ethoxyethanol, 2-methoxypropanol, 2-butoxypropanol, toluene, xylene, cumene, tetrahydrofuran, dioxane, acetone, methylethyl ketone, methylisobutyl ketone, cyclohexanone, and combinations thereof.

The polymerization of the ethylenically unsaturated monomers with the unsaturated dicarboxylic acid anhydride reaction product is conveniently conducted in the presence of a free radical catalyst such as organic peroxides, azo compounds, combinations thereof and the like. Particularly suitable catalysts include, for example benzoyl peroxide, t-butylperbenzoate, di-tert-butylperbenzoate, t-butylperoctoate, azobisisobutyronitrile t-butylazo-2-cyano-4-methyl pentane, t-butylazo-4-cyanovaleric acid, t-butylazo-2-phenyl-4-methyl pentane, t-butylazo-2-phenyl propane, 1-cyano-1-(t-buty-lazo)-cyclohexane, 2-t-butylazo-1, 1-diethoxycarbonyl-2,4-dimethyl pentane, and combinations thereof.

Suitable epoxy resins which can be employed herein include any epoxy resin having an average of more than one 1,2-epoxide group per molecule and an average of from zero to 30, preferably from 4 to 20 aliphatic hydroxyl groups per molecule. The higher aliphatic hydroxyl-containing epoxy resins can be conveniently prepared by reacting a relatively low equivalent weight epoxy resin having an average of more than one 1,2-epoxy group per molecule with a material having an average of more than one hydroxyl group per molecule. Particularly suitable epoxy resins include those prepared by reacting a diglycidyl ether of an aromatic dihydroxyl-containing compound with an aromatic dihydroxyl-containing compound. Most suitable aromatic dihydroxyl-containing compounds include those represented by the formulas



(I)



(II)

wherein A is a divalent hydrocarbyl group having from 1 to 12, preferably from 1 to 6, carbon atoms, -O-, -S-, -S-S-, $-\overset{O}{\overset{\|}{S}}-$,

$$-\overset{O}{\overset{\|}{S}}-, \text{ or } -O-\overset{O}{\overset{\|}{C}}-O-,$$

each X is independently hydrogen, a hydrocarbyl or hydrocarbyloxy group having from 1 to 10, preferably from 1 to 4, carbon atoms, or a halogen atom, preferably chlorine or bromine and n has a value of zero or 1. Most suitable such dihydroxyl-containing compounds include, for example, bisphenol A, bisphenol F, resorcinol, catechol, hydroquinone, halogenated or alkyl or alkoxy substituted derivatives of such dihydroxyl-containing compounds, and combinations thereof. These dihydroxyl-containing compounds can be the same or different from those from which the epoxy resin was prepared. Said epoxy resins can be prepared by dehydro-halogenating the reaction product of a dihydroxyl-containing compound with an epihalohydrin such as epichlorohydrin, epibromohydrin, epiiodohydrin as well as alkylated derivatives thereof such as, for example, methylepichlorohydrin, methylepibromohydrin, methylepiiodohydrin, and combinations thereof.

Suitable monoalkanoloamines which can be employed herein include, for example, those represented by the formula

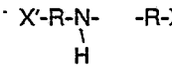
$X'\text{-}R\text{-}NH_2$ (III)

wherein R is a divalent hydrocarbyl or hydrocarbyloxy group having from 2 to 9 carbon atoms and X' is hydroxyl.

Particularly suitable primary amines which can be employed herein include, for example, ethylamine, propylamine, butylamine, aniline, benzylamine, ethanolamine, methoxyethylamine, methoxypropylamine, ethoxyethylamine, ethoxypropylamine, ethoxybutylamine, butoxyethylamine, butoxypropylamine, butoxybutylamine, nitrobenzylamine, and combinations thereof.

The term hydrocarbyl as employed herein means any aliphatic, cycloaliphatic, aromatic, aryl substituted aliphatic or aliphatic substituted aromatic groups.

Suitable dialkanolamines which can be employed herein include, for example, those represented by the formula



(IV)

wherein each X and R are independently as defined above.

Particularly suitable secondary amines which can be employed herein include, for example, diethylamine, dipropylamine, dibutylamine, diethanolamine, methylethanolamine, ethylethanolamine, bis-(methoxyethyl)amine, bis(ethoxyethyl)amine, bis(methoxypropyl)amine, bis(butoxyethyl)amine, bis(butoxy-propyl)amine, bis(butoxybutyl)amine, and combinations thereof.

Suitable phenols include besides phenol, those substituted with hydrocarbyl groups having from 1 to 10 carbon atoms, halogen atoms, particularly chlorine or bromine, and the like. Particularly suitable phenols include, for example, phenol, o-cresol, nonylphenol, chlorophenol, dichlorophenol, trichlorophenol, bromophenol, dibromophenol, tribromophenol, butylphenol, and combinations thereof.

Suitable ethylenically unsaturated dicarboxylic acid anhydrides which can be employed herein include, for example, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, citraconic anhydride, itaconic anhydride, dodecenylsuccinic anhydride, maleic anhydride adducts of linoleic acid, cyclopentadiene or methylcyclopentadiene, combinations thereof and the like.

The carboxylic acid anhydride is added to the modified epoxy resin at a temperature of not greater than 100°C, preferably not greater than 75°C. At temperatures greater than 100°C, too much of the anhydride undesirably reacts with the aliphatic hydroxyl groups instead of the secondary amine groups resulting from the reaction between the epoxy resin and the primary amine compounds.

Suitable polymerizable ethylenically unsaturated compounds which can be employed herein include, for example, styrene, alpha-methylstyrene, halogenated styrene, butadiene, alkyl or hydroxyalkyl acrylates, alkyl or hydroxyalkyl methacrylates, acrylic acid, methacrylic acid, acrylonitrile, methacryilonitrile, vinyl chloride, vinylidine chloride, vinyl acetate, methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, isoprene, isobutylene, chloroprene, hydroxypropyl acrylate, hydroxyethyl acrylate, hydropropyl methacrylate, hydroxyethyl methacrylate, acrylamide, maleic acid, fumaric acid, itaconic acid, citaconic acid, mesaconic acid, and combinations thereof.

Suitable bases which can be employed to neutralize the amide modified epoxy resins of the present invention include, for example, amines, alkali metal and alkaline earth metal hydroxides. Particularly suitable bases include, sodium hydroxide, potassium hydroxide, lithium hydroxide, calcium hydroxide, barium hydroxide, magnesium hydroxide, ammonia, butylamine, dibutylamine, triethylamine, tributylamine, dimethylethanolamine, methyldiethanolamine, N-methylmorpholine, and combinations thereof.

Suitable curing agents which can be employed in the coating compositions with the amide modified epoxy resins include, for example, melamine-aldehyde resins, alkylated melamine-aldehyde resins, urea-aldehyde resins, alkylated urea-aldehyde resins, phenol-aldehyde resins, alkylated phenol-aldehyde resins, blocked isocyanates, and combinations thereof. Particularly suitable curing agents include, for example, hexamethoxymethyl-melamine, commercially available as CYMEL™ 303 from American Cyanamide Co., BEETLE™ 65, a methylated urea-formaldehyde resin commercially available from American Cyanamide Co., VARCUM™ 1131, a phenolic-type resin, commercially available from Reichhold Chemicals, Inc., and combinations thereof.

If desired, catalyst promoters or accelerators can be employed. Suitable such promoters or accelerators include, for example, mineral and organic acids, combinations thereof and the like. Particularly suitable such accelerators or promoters include, for example, phosphoric acid, polyphosphoric acid, organic sulfonic acids such as, for example, benzene sulfonic acid, toluene sulfonic acid, and combinations thereof.

Suitable solvents which can be employed to prepare solvent borne coatings from the compositions of the present invention include those solvents mentioned above as a reaction medium.

Various additives such as, for example, pigments, dyes, flow control agents, fillers and the like can be added to the coating compositions if desired.

The following examples are illustrative of the invention.

EXAMPLE 1

To a four-neck one liter reaction vessel equipped with a means for nitrogen purging, temperature control, stirring, condensing and reactant addition were added 100 parts by weight, pbw, (0.056 equiv.) of a diglycidyl ether of bisphenol A having an average epoxide equivalent weight of 1800 and 34 pbw of 2-butoxy ethanol. The contents were heated to a temperature of 120°C and 4.91 pbw (0.047mole) of

diethanolamine was added and the reaction maintained at a temperature of 120°C for 30 minutes. Then 0.51 pbw (0.0084 mole) of monoethanolamine was added and the reaction continued at 120°C for 30 minutes. The temperature was then cooled to 75°C and 0.81 pbw (0.0083 mole) of maleic anhydride was added. The temperature was maintained at 75°C for 30 minutes. The temperature was adjusted to 100°C and a mixture containing 19.39 pbw (0.19 mole) of styrene, 17.07 pbw (0.20 mole) of methacrylic acid and 0.36 pbw of azobisisobutyronitrile was slowly added over a period of 1 hour. After adding a mixture of 0.08 pbw of azobisisobutyronitrile and 11.6 pbw of n-butanol, the polymerization was continued at 100°C for 30 minutes. The temperature was adjusted to 75°C and a mixture of 14.58 pbw (0.16 mole) of diethanol amine and 375 pbw of deionized water was added over a period of 1 hour to neutralize the acid groups contained in the reaction product. The reaction was conducted at 75°C for 30 minutes. The resultant product had a non-volatiles content of 21.2% by weight and a Brookfield viscosity of 2800 cps (2.8 Pa•s) at 25°C and pH of 8.6.

EXAMPLE 2

A coating was prepared by blending 38 pbw of the amide modified epoxy resin prepared in example 1 at 21% by weight non-volatiles, 0.9 pbw of hexamethoxymethyl melamine (commercially available from American Cyanamid as Cymel™ 303) and 0.44 pbw of p-toluene sulfonic acid as a catalyst promoter.

This coating was applied to unpolished cold rolled steel panels via a No. 6 Meyer wound wire rod to provide a coating thickness of 0.4 mil (0.01 mm). The coated panels were baked in an oven at 310°F (154°C) for 10 minutes. The following tests were performed on the resultant coated panels.

MEK RESISTANCE

--A two pound (0.9 kg) ball peen hammer with the ball end covered with eight layers of cheese cloth was saturated with methyl ethyl ketone (MEK) and rubbed across the baked panels. One back and forth cycle across the panel was considered a being 1 MEK double rub. One hundred double rubs were considered a pass.

ACID RESISTANCE

--Glacial acetic acid, 1 ml, was placed on the coating and a timer started. When the coating delaminates from the substrate, failure has occurred and the timer stopped. This time is recorded and referred to as time to failure for glacial acetic acid.

BOILING WATER RESISTANCE

--A coated panel was immersed in boiling water for 60 minutes. The panel was then removed and cut through with an eleven blade cross hatch knife with 1.5 mm spacing. A strip of cellophane tape was applied to the scratched surface and the tape was then pulled off. No loss of adhesion was noted as a pass.

IMPACT RESISTANCE

--The coated panel was impacted with a falling weight from a calibrated height to give an impact up to 180 in.-lb (20.34 J). An HCl-$CuSO_4$-water solution was applied to the impact spot for 5 minutes to check for failure.

FLEXIBILITY

--A coated panel was bent from 0 to 1/8 in. (0 to 3.2 mm) using a wedge mandrel attachment with a Gardner impacter. The bent panel was checked for failure with the HCl-$CuSO_4$-water solution. Any failure was noted and recorded as percent failure from the smaller end. One inch (25.4 mm) of failure or less was considered a pass.

PENCIL HARDNESS

--This was determined by the procedure defined in Paint Testing Manual by H. A. Gardner and G. G. Sward in the 12th Ed. (1962), pp 131-132. When the coating is broken to the metal surface, that constitutes a failure. The results reported here are a pencil hardness that does not break the film, but the next pencil grade does break the film.

The results are given in the following table.

FILM PROPERTIES	RESULTS
MEK double rubs	Pass
Reverse Impact, in-lbs/J	No Failure, (>180/20.34)
Boiling Water Resistance. 60 min	Pass
Chemical Resistance, min./	25
Pencil Hardness	4H
Film Thickness, mils/mm	0.4/0.01

Claims

1. A curable amide modified epoxy resin prepared by reacting the reaction product of (A) the reaction product of (1) at least one epoxy resin having an average of more than one 1,2-epoxy group per molecule and an average of from zero to 30 aliphatic hydroxyl groups per molecule and (2) (a) at least one dialkanolamine and (b) at least one monoalkanolamine wherein components (a) and (b) are added as a mixture or sequentially with component (a) being added first; with (B) at least one anhydride of a saturated or an ethylenically unsaturated dicarboxylic acid; and wherein the components are employed in quantities which provide

(i) a ratio of moles of component (A-2-a) to epoxy equivalent contained in component (A-1) of from 0.55:1 to 0.95:1;

(ii) a ratio of moles of component (A-2-b) to epoxy equivalent contained in component (A-1) of from 0.05:1 to 0.45:1;

(iii) a ratio of combined moles of components (A-2-a) and (A-2-b) per epoxy equivalent in component (A-1) of from 0.9:1 to 1.45:1; and (iv) a ratio of moles of component (B) to moles of component (A-2-b) of from 0.75:1 to 1:1.

2. A curable amide modified epoxy resin of Claim 1 wherein

(i) component (A-1) is a diglycidyl ether of bisphenol A or a halogenated or alkyl ring substituted derivative thereof; and;

(ii) component (B) is an unsaturated dicarboxylic acid anydride.

3. A curable amide modified epoxy resin of Claim 2 wherein

(i) component (A-1) has an average of from about 4 to about 20 aliphatic hydroxyl groups per molecule;

(ii) component (A-2-a) is diethanolamine;

(iii) component (A-2-B) is monoethanolamine; and

(iv) component (B) is maleic anhydride.

4. A curable amide modified epoxy resin prepared by polymerizing (I) the reaction product of (A) the reaction product of (1) an epoxy resin having an average of more than one 1,2-epoxy group per molecule and an average of from zero to 30 aliphatic hydroxy groups per molecule and (2) (a) a dialkanolamine and (b) a monoalkanolamine wherein components (a) and (b) are added as a mixture or sequentially with component (a) being added first; with (B) an anhydride of an unsaturated dicarboxylic acid; with (II) a polymerizable ethylenically unsaturated monomer or mixture of monomers; wherein

(i) the ratio of moles of component (I-A-2-a) to epoxy equivalent contained in component (I-A-1) is from 0.5:1 to 0.95:1;

(ii) the ratio of moles of component (I-A-2-b) to epoxy equivalent contained in component (I-A-1) is from 0.05:1 to 0.5:1;

(iii) the ratio of combined moles of components (I-A-2-a) and (I-A-2-b) per epoxy equivalent contained in component (I-A-1) is from 0.9:1 to 1.5:1;

(iv) the ratio of moles of component (I-B) to moles of component (I-A-2-b) is from 0.75:1 to 1.25:1; and

(v) component (II) is present in a quantity which provides from 5 to 75 percent by weight of component (II) based upon the combined weight of components (I) and (II).

5. A curable amide modified epoxy resin of Claim 4 wherein

(i) component (I-A-1) is a diglycidyl ether of bisphenol A or a halogenated or alkyl ring substituted derivative thereof;

(iv) component (II) is a vinyl substituted aromatic compound, alkyl ester or hydroxyl or hydroxyalkyl ester of acrylic or methacrylic acid, acrylic acid or methacrylic acid or a combination thereof and is present in a quantity which provides from about 15 to about 30 percent by weight component (II) based upon the combined weight of components (I) and (II).

6. A curable amide modified epoxy resin of Claim 5 wherein

(i) component (A-1) has an average of from about 4 to about 20 aliphatic hydroxyl groups per molecule;

(ii) component (I-A-2-a) is diethanol amine;

(iii) component (I-A-2-b) is monoethanolamine;

(iv) component (I-B) is maleic anhydride; and

(v) component (II) is a mixture of styrene, at least one of acrylic or methacrylic acid and at least one of hydroxyethyl acrylate, hydropropyl acrylate, hydroxyethylmethacrylate or hydroxypropyl methacrylate.

7. A composition resulting from neutralizing a curable amide modified epoxy resin of any one of Claims 1 to 6 with a base.

8. A composition of Claim 7 wherein said base is an amine or a hydroxide of an alkali metal or an alkaline earth metal.

9. A coating composition comprising an amide modified epoxy resin of any one of Claims 1 to 8 and a curing agent therefor.

10. A coating composition of claim 9 wherein said curing agent is hexamethoxymethylmelamine.